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In pursuit of high-force/high-stroke conducting polymer actuators

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ABSTRACT

Conducting polymer actuators are being investigated for a number of applications. Both linear contracting/expanding and bending type actuators can be constructed that utilise the redox-induced volume changes in the conducting polymer. Improved actuator performance has been demonstrated by modifications to our helix-tube design. The pitch of the helix and bundling the actuators have increased the strain and force generated. Short-term improvements to the strain were also generated using new dopants, but cycle life was poor in this case. Further studies on the mechanism of actuation have continued to focus attention on the influence of the elastic modulus on the actuation strain. Surprising results have been obtained from polythiophene actuators that show an increased strain and increased work-per-cycle with an increasing applied load in isotonic operation. The observations were explained by an increase in modulus during the contraction cycle of the actuation. Preliminary studies show how the change in modulus can be conveniently measured using an *in situ* mechanical technique.

Keywords: conducting polymers, polypyrrole, polyaniline, polythiophene, helix tube, fibre, modulus.

1. INTRODUCTION

Applications for low-voltage actuators extend through several areas of technology: robotics and machine parts to devices for assisting human movement and biomedical applications. We have been involved in the development of conducting polymer actuators for applications including an electronic Braille screen [1], cochlear implant [2], rehabilitation glove [3] and gas valve system[4]. These and other applications demand higher actuation performance than that currently available from artificial muscles. We have concentrated our research in the area of low-voltage actuation materials that operate in an electrochemical cell. This paper reviews some of our recent progress in the developing the technology of conducting polymer actuators and in the understanding of the underlying principles.

Much of our work has focussed on "polypyrrole helix tube" actuators, although we also present in this paper the application of the helix tube design to polythiophene. The helix tube actuator consists of a hollow polymer fibre that contains a helically wound platinum wire in the wall of the tube to facilitate efficient electrochemistry along the entire length of the material and without impeding greatly the mechanical deformation induced by the polymer oxidation / reduction. The helix tube design is described in the paper by Ding et al[1]. The initial results showed a very large increase in actuation rate as a result of producing the helix tube geometry as compared with a regular flat film. In combination with the resistance compensation technique (introduced to conducting polymer actuators by Madden et al [5]) and using a polypyrrole auxiliary electrode, peak strain rates of 13%/s were demonstrated for the polypyrrole helix tube actuators. A similar helix tube design has been used by Kaneto et al to produce polypyrrole actuators generating 11% strain [6]. We report in this paper the effect of helix pitch angle on the actuation performance as well as high force generation obtained by bundling helix tubes.

In terms of understanding the basic mechanisms of actuation in conducting polymers, we have focussed our attention on the influence of the elastic modulus on the strain generated. As shown in several papers [3, 7-13], the modulus of

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polypyrrole changes during redox cycling and this change in stiffness translates into reversible "actuation"- ie. movement and/or force generation. In the isotonic situation illustrated in figure 1a), the actuation is arbitrarily reduced to 3 separate steps:

1. Initial elastic stretching caused by the load application (A→ B in Fig. 1; usually ignored in actuator studies)
2. Reversible length change due to electrochemistry (B→ C in Fig. 1; due to ion movements, osmosis etc.)
3. Reversible length change due to a change in elastic modulus (C→ D in Fig. 1)

Assuming that the behaviour is Hookean and that the cross-sectional area A does not change greatly during redox cycling, the actuation strain (ε_f) at an applied force f is given by:

$$\varepsilon_f = \varepsilon_0 + \frac{f}{A}\left(\frac{1}{Y'} - \frac{1}{Y}\right) \qquad (1)$$

where ε_0 is the actuation strain at zero applied load; and Y and Y' are the Young's moduli before and after the voltage stimulus is applied, respectively. The predicted responses for isotonic actuation are shown in Figure 1b) for different ratios of Y:Y'.

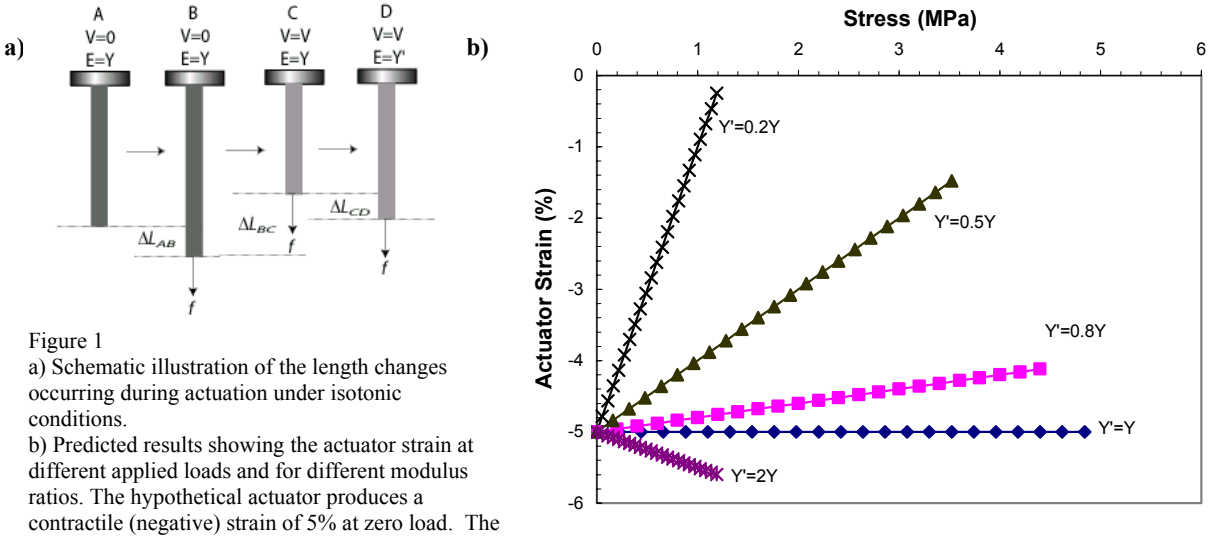

Figure 1
a) Schematic illustration of the length changes occurring during actuation under isotonic conditions.
b) Predicted results showing the actuator strain at different applied loads and for different modulus ratios. The hypothetical actuator produces a contractile (negative) strain of 5% at zero load. The initial modulus (Y) is taken as 0.1 GPa.

As shown in Fig. 1b) the actuator strain is unchanged when the modulus does not change. However, the actuation strain decreases for the case where the modulus decreases when the voltage stimulus is applied. In the case analysed, the actuator operates by contraction (negative strain), which is partially offset due to lengthening resulting from the decrease in modulus. The latter effect is proportional to the applied load, so that at sufficiently high loads the actuation strain becomes zero. It is also possible for the actuation strain to increase with applied load. This occurs for contractile actuators when the modulus increases with the application of the stimulating voltage. We show in this paper, the first demonstration of this "positive feedback" effect. Previous work has validated the above model for polypyrrole films [10].

2. MATERIALS AND METHODS

Propylene carbonate (PC) (Aldrich) and tetrabutylammonium hexafluorophosphate (TBA-PF_6, obtained from Sigma) both of AR grade were used. Pyrrole monomer from Merck was distilled and stored under −18 ◦C before use. Thiophene was obtained from Sigma-Aldrich**.** Platinum wires in 250 and 50 µm diameter were from Goodfellow. The constant current required for polymerization was measured using an EG and G Princeton Applied Research Model 363 potentiostat / galvanostat.

PPy fibre was grown galvanostatically for 16 hours with a 0.15 [mA/cm^2] current density. Polymerization solution was PC containing 0.06M Pyrrole and 0.05M TBA-PF_6. The polymerization temperature was controlled around −25 to −28 °C. A two-electrode configuration was used; the working electrode was 250µm Pt wire tightly wound by 50µm Pt wire as helix; the auxiliary electrode was a stainless steel mesh. After growth, the 250µm Pt wire was pulled out leaving a hollow PPy fibre containing the thinner Pt wire embedded as a helix in the tube wall. Two pieces of 250µm Pt wire were inserted to each end of PPy helix tube to enable electrical connection and sealed by hot-melt polystyrene. PPy helix tubes were stored wet in PC containing 0.25M TBA-PF_6 before testing. Figure 2 shows the actuator structure; further fabrication information is given in reference[1]. Polythiophene actuators were prepared in an identical manner.

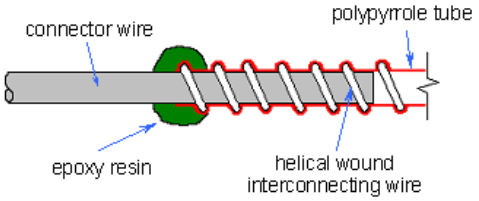

Fig.2. Structure of PPy helix tube actuator.

Figure 3 shows the arrangement of the test cell. The test cell consists of an actuator, which is connected as the working electrode, a counter electrode, an electrolytic solution, and a glass tube to contain everything. The tube is clamped in a position that is fixed relative to the lever-arm unit. One end of the actuator is fixed to the bottom end of the tube and the other end is connected to the lever arm and is free to move.
The reference electrode was Ag wire in 0.01M $AgNO_3$ and 0.1M TBA.PF_6 in acetonitrile (ACN) using 0.1M TBA.PF_6 in PC as a salt bridge.

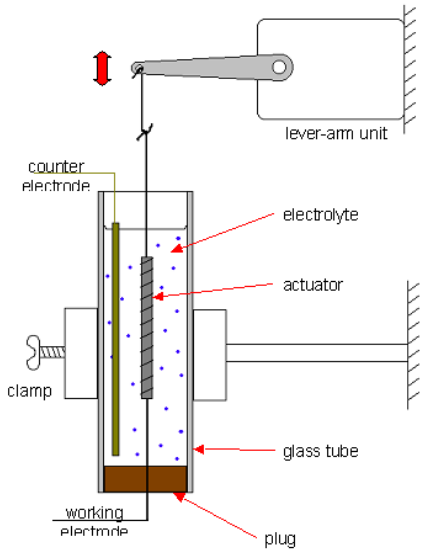

Fig.3.Test cell for actuators.

3. RESULTS

Polypyrrole Helix Tube Actuators
The pitch of the helically wound platinum wire was investigated for its affect on actuation performance. Several samples were prepared with the pitch in the range 10-12 turns/mm or 1-2 turns/mm. As shown in Figure 4, the tighter pitch produces a significantly increased strain when tested under identical conditions. The improved performance was attributed to both increased electrochemical efficiency induced by the shorter distances between the PPy and the Pt interconnect. In addition, the tighter pitch wire has a significantly reduced stiffness. The lower stiffness of the interconnecting wire will impede the actuation process less and, therefore, allow a greater strain to be generated. Recently, Kaneto and co-workers have shown that a similar PPy helix tube actuator with an even smaller pitch produced even larger strains (up to 11%)[6]

This same research group has also reported recently the highest linear strain from PPy at 26% [14]. These high strains were produced using novel dopants. We have repeated these works using the helix tube as the basic structure. Thus, PPy doped with tertiary butyl ammonium bis(trifluoromethanesulfonyl)imide (TBA.TFSI) was prepared from methyl benzoate solution galvanostatically. The actuation results of the PPy.TFSI helix tube tested in aqueous LiTFSI (1 M) are shown in Figure 5. Large strains of 14.5% were observed in the first cycle (isotonic, fixed load of 0.18 MPa), but the strain rapidly decreased with subsequent cycles to 10%, 4.8% and 3.8%. Similar samples were tested in other electrolytes, but were also found to show poor cycle lifetime.

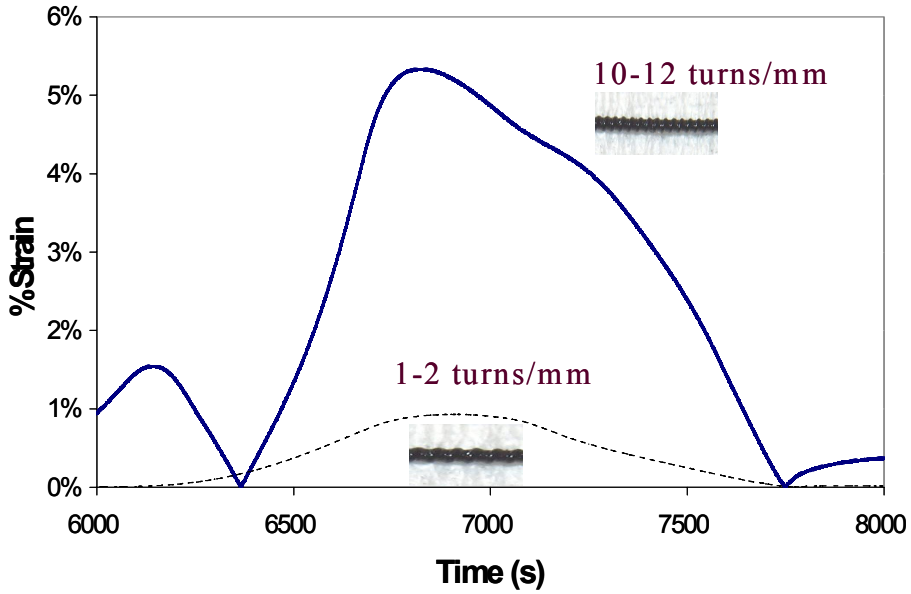

Figure 4 Actuation strain obtained under isotonic conditions during voltage cycling between –1.5 and +1.5V (vs. Ag/Ag^{+}) at 2 mV/s. Sample a) is a $PPy.PF_6$ helix tube with a pitch of 1-2 turns/mm and b) has a pitch of 10-12 turns/mm.

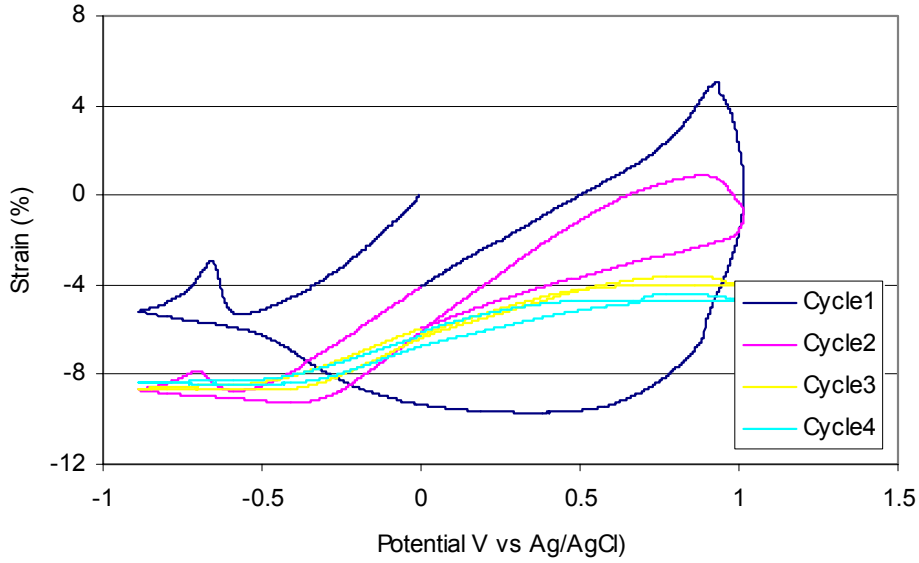

Figure 5 Actuation strain obtained under isotonic conditions during voltage cycling between –0.9 and +1.0V (vs. Ag/AgCl) at 0.2 mV/s. The sample is a PPy.TFSI helix tube with a pitch of 1-2 turns/mm and was tested in 1M LiTFSI (aq) electrolyte.

Bundled fibres for higher force capacity

The analysis above shows that an obvious way to produce higher strains at a given isotonic load is to reduce the applied stress by increasing the cross-sectional area. Bundled fibres are the preferred geometry, since the cross-sectional area can be increased without increasing thickness, which increases diffusion distances and slows down the actuation. Figure 6 compares the isotonic strain generated by a single helix tube (sample A) and a multi-helix tube parallel assembly

(sample B). The 4-fiber assembly shows the same strain at low loads, but higher strains at higher preloads than the single fiber. As seen from equation (1), the higher cross-sectional area (*A*) for the 4-fiber assembly accounts for the slower decrease in actuator strain at higher loads compared with the single fiber (small *A*). An additional advantage of the multi-parallel fiber assembly for high force applications is that it can sustain higher loads before failure than the single fiber. Again this is due to a higher cross-sectional area resulting in lower applied stress.

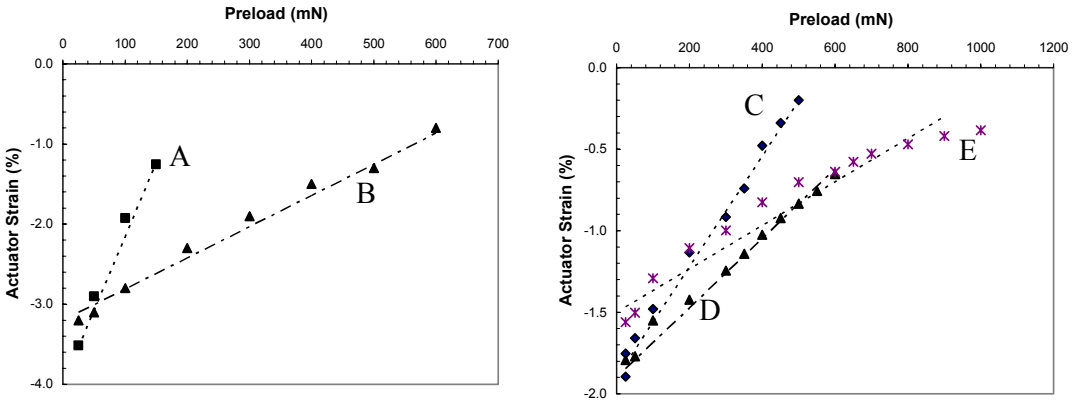

Figure 6 Isotonic strain measured from A) single helix tube; B) 4-helix tube parallel assembly; C) D) and E) are multi-helix tube bundles described in the text.

A problem with the parallel fibre assembly was the equal tensioning of all fibres. If one fiber were tensioned less than the other fibers, then that fiber's contribution to the actuation would be reduced. The problems associated with achieving equal tensioning of all fibers within the system was found to be a major difficulty in producing high force actuators from parallel fiber. A more reliable means for producing multi-helix assemblies, with all fibers in near equal tension, was therefore sought and two related methods are described in this section. Firstly, a multi-helix bundle was formed by wrapping a platinum wire helically around two PPy coated helix tubes (sample C). Secondly, a platinum-wrapped double helix bundle was coated in PPy (sample D). Sample E was prepared by taking two sample D specimens, bundling and wrapping these with Pt wire then polymerizing that bundle with PPy. Sample E therefore comprised 4 helix tubes, and a total of 7 PPy coated Pt helices.

The actuator strains measured under isotonic conditions for the multi-helix bundles are also shown in Figure 6. The maximum strain obtained from these samples was slightly less than 2%, which is significantly lower than the single helix (~3%). The lower strain may be due to the additional PPy coated Pt helices that could restrict movement. The major benefit of the multi-helix bundles is seen in the higher loads that can be sustained – Sample E producing 0.4 % strain at preloads of 1000 mN. A similar 9-fiber sample was also constructed and found to give ~0.5% strain at 2000 mN. Previous reports have only demonstrated appreciable isotonic strains from PPy at loads of 250 mN [11], 450 mN [10] and 800 mN [15].

Polythiophene Helix Tube Actuators

Polythiophene helix tube actuators have also been prepared as for the PPy samples. As shown in Figure 7, the isotonic strain is strongly dependent upon the actuation electrolyte. In propylene carbonate (with t-butyl ammonium hexafluorophosphate) the strain decreases from 1.5% at low loads to zero at 2.5 MPa. A lower strain of 0.4% was obtained at low loads in an ionic liquid electrolyte. However, the strain increased with increasing load to around 0.6% at 4 MPa (the breaking load). An increase in strain with increasing load had not been previously reported for conducting polymer actuators, although is theoretically possible as described above. Measurement of the modulus before and after voltage stimulation in both electrolytes confirmed the modulus shift effect, as shown by the dashed lines in Fig. 7. The reasons for the different moduli in different electrolytes are yet to be determined but are likely due to the degree of swelling (influencing the concentration of elastically active network chains) and the degree of ionisation (influencing the interchain bonding and chain stiffness).

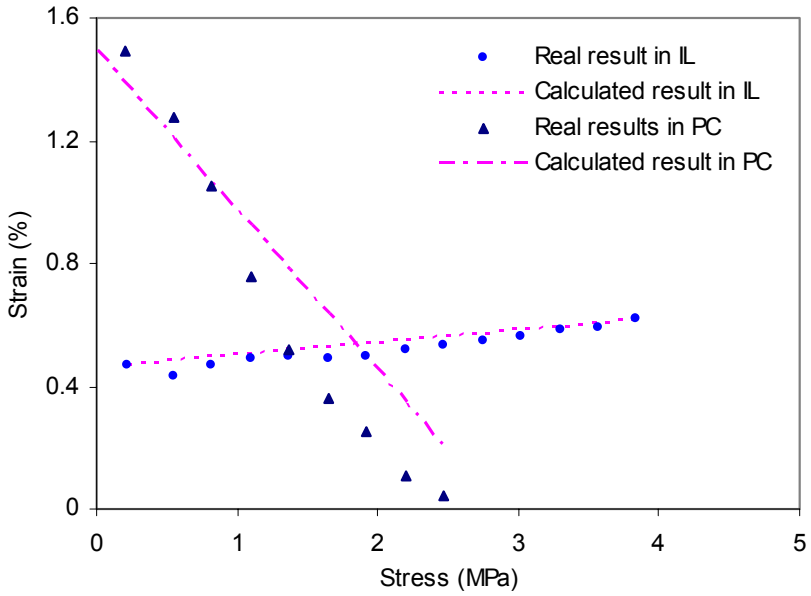

Figure 7
Measured and calculated actuation strain for poly(3-methyl thiophene) doped with PF_6 and tested in 2 different electrolytes. Calculated values determined using equation (1).

In-situ measurement of modulus

Following the work of DeRossi and co-workers [16], we have developed a system for evaluating the modulus of the actuator during actuation. A small force oscillation was applied continuously during actuation testing and the resultant strain analysed to give the stiffness coefficient (K_1- related to modulus). Figure 8 shows this modulus variation along with the cyclic voltametric diagram, showing the relationship between electrochemistry and mechanical properties. During oxidation of the PPy.PF_6 in propylene carbonate electrolyte containing TBA.PF_6, the modulus initially increases presumably due to increased ionisation of the chains producing increased interchain bonding and intrachain stiffness. At higher voltages (or longer times in the oxidised state) the stiffness decreases significantly, which may be due to the continued swelling of the polymer resulting from osmotic pressure. The swelling reduces the concentration of elastically active network chains, so that the modulus decreases. The modulus continues to decrease during the cathodic scan until the reduction reaction reduces the charge on the polymer and reverses the osmotic pressure. Figure 9 shows that increasing the frequency of applied voltage decreases the significance on stiffness variation. At slower scan speeds the osmotic process occurs at a similar rate to the redox reactions, so that the initial increase in modulus is less prominent.

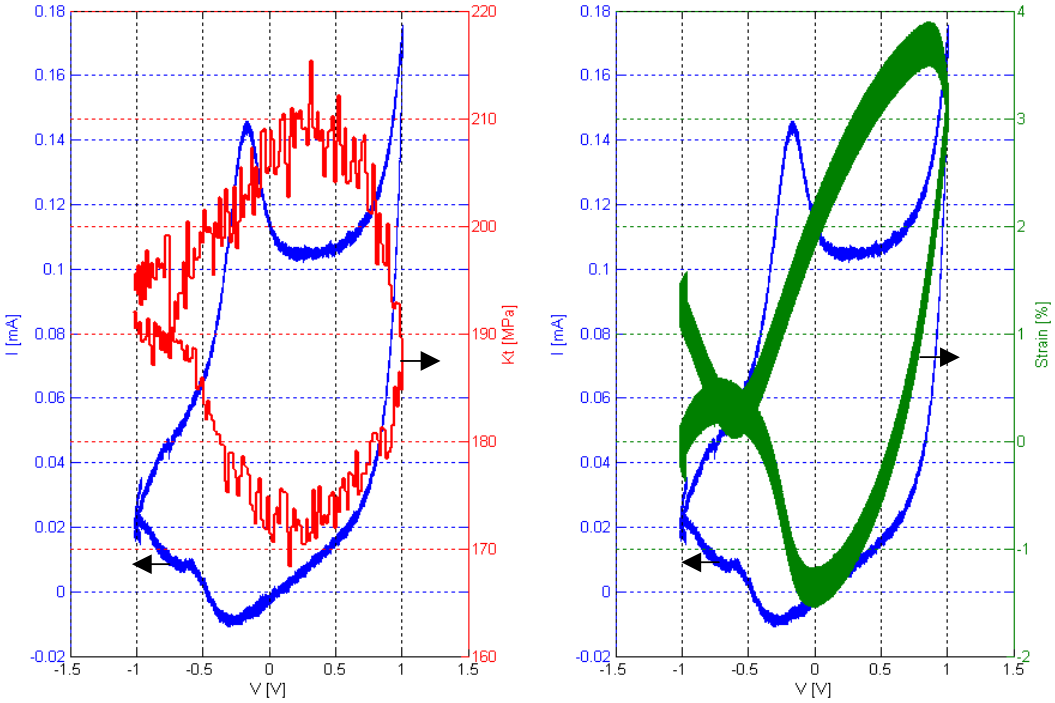

Figure 8 CV diagram and stiffness changing during actuation.

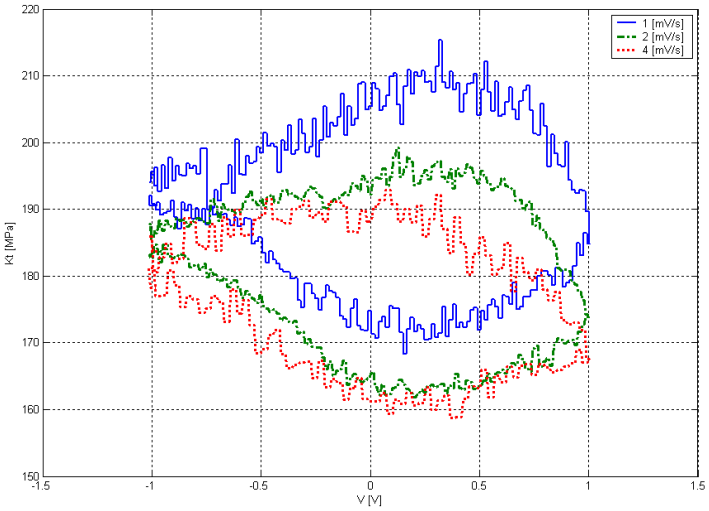

Fig.ure 9. Stiffness variation during actuation in different scan rates.

4. CONCLUSIONS

Recent studies in our group have improved the performance of conducting polymer actuators and contributed to their better understanding. In terms of the technology, we have shown that increased pitch of the helix wire increases the strain obtained from polypyrrole helix tube actuators. We have also produced reasonable actuation strains at higher applied forces by using multiple helix tubes. In other studies, we have confirmed that certain dopants can intrinsically produce higher strains although in our work the cycle life was poor.

Our understanding of basic mechanisms has continued to focus on the effect of modulus shift during voltage stimulation on the actuation performance. We show for the first time that an increase in strain can be obtained at higher isotonic loads. This observation was made for polythiophene helix tubes operated in an ionic liquid electrolyte. The increased strain results from a lower modulus coinciding with the expanded (reduced) state for this polymer. In all previous systems studied the modulus was higher in the expanded state so that the actuation strain decreased with increasing applied load. *In situ* measurements of modulus during redox cycling has also shown some interesting trends that may be related to the intrinsic mechanisms of charging and osmosis. Our preliminary results in this area are the subject of on-going studies.

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